# DRAFT SF 298

| | | |
|---|---|---|
| 1. Report Date (dd-mm-yy) | 2. Report Type | 3. Dates covered (from... to ) |

| | |
|---|---|
| 4. Title & subtitle<br>Ion Beam Enhanced Deposition as Alternative Pretreatment for Adhesive Bonding of Aircraft Alloys<br>Tri-Service Committee on Corrosion Proceedings | 5a. Contract or Grant # |
| | 5b. Program Element # |
| 6. Author(s)<br>Dr. Gerhardus H. Koch<br>Dr. Arnold H. Deutchman | 5c. Project # |
| | 5d. Task # |
| | 5e. Work Unit # |
| 7. Performing Organization Name & Address | 8. Performing Organization Report # |
| 9. Sponsoring/Monitoring Agency Name & Address<br>Tri-Service Committee on Corrosion<br>USAF WRIGHT-PATTERSON Air Force Base, Ohio 45433 | 10. Monitor Acronym |
| | 11. Monitor Report # |

12. Distribution/Availability Statement
Approved for Public Release
Distribution Unlimited

13. Supplementary Notes

14. Abstract



15. Subject Terms
Tri-Service Conference on Corrosion

| Security Classification of | | | 19. Limitation of Abstract | 20. # of Pages | 21. Responsible Person (Name and Telephone #) |
|---|---|---|---|---|---|
| 16. Report | 17. Abstract | 18. This Page | | | |

# TRI-SERVICE CONFERENCE ON CORROSION



**21-23 JUNE 1994**

**SHERATON PLAZA HOTEL**
**ORLANDO, FLORIDA**

# PROCEEDINGS

# Ion Beam Enhanced Deposition as Alternative Pretreatment for Adhesive Bonding of Aircraft Alloys

Dr. Gerhardus H. Koch*
CC Technologies
2704 Sawbury Blvd.
Columbus, OH 43204-1821

and

Dr. Arnold H. Deutchman
BeamAlloy Corporation
6360 Dublin Industrial Lane
Dublin, OH 43017-3241

## ABSTRACT

Surface treatment of aluminum alloys based on wet chemical processes is subject to increasing regulations. The objective of the work described in this paper was to demonstrate the feasibility of applying a non-chemical technique to generate an aluminum oxide surface with adhesive bonding properties comparable to that generated with the traditional technique. This paper describes the use of ion beam enhanced deposition which meets the objective of this work.

## INTRODUCTION

Adhesively bonded structures are being used extensively as structural components for both military and civilian aircraft. Proper surface treatment is essential in order to achieve a good bonding surface that can be the basis for high strength adhesive bonds with good durability in corrosive environments. Surface treatments based on wet chemical processes have been shown to create excellent surfaces for adhesive bonding and coating application. The most common surface treatments

used in the United States are: (1) the Forest Product Laboratory (FPL) process for pickling, and (2) the Phosphoric Acid Anodizing (PAA) process.

The state-of-the-art surface pretreatments for adhesive bonding and organic coatings contribute to high strength and durable adhesive bonds. However, Environmental Protection Agency (EPA) regulations impose increasingly strict limitations on the wet chemical surface preparation processes. Particularly, surface treatment processes such as pickling and anodizing which rely on wet chemistry techniques and are large water users, are subject to regulations.

In order to find replacements for the wet chemical surface treatment techniques, a research program was initiated to develop alternative non-chemical techniques that do not produce waste detrimental to health and environment, and are compliant with present and future EPA regulations. An important requirement for such a technique is that it produces surfaces that result in mechanical strength and durability equal to or better than those produced by the wet chemical methods. In order to achieve the objective of this research program, a physical coating technique based on ion implantation was applied.

## BACKGROUND

Research into the area of surface treatment of aluminum alloy components for purposes of adhesive bonding appears to have started in the 1950's, where surface preparation methods were developed primarily through an empirical approach[1]. The main increase in research activity and development occurred in Europe and the United States during the 1970's and early 1980's, where researchers suggested that the macroscopic surface morphology, and surface oxide structure and composition are important for the bondability of aluminum alloys[2-6]. In the early 1970's, research was concentrated on mechanical strength and durability testing of adhesive bonds, and the relationship between adhesive bond strength and surface treatment. By the early 1980's, the technology of adhesive bonding was fairly well established, but research into the mechanism of adhesion and adhesive bond failure continued.

## Aluminum Oxide Structure And Morphology

Some of the significant features of aluminum oxides were recognized as early as 1953. Keller and coworkers[1] described the basic structure of anodic aluminum oxide films as consisting of close-packed cells of oxide, predominately hexagonal in shape, each of which contains a single pore. Much later in the 1970's and early 1980's, transmission electron microscopy (TEM)[2] and scanning transmission electron microscopy (STEM)[7,8] analyses were used to gain a better understanding of the surface oxide morphology and how the various morphological differences could affect bondability and durability of adhesive bonds of aluminum alloys.

The most common anodizing pretreatments for adhesive bonding of aluminum alloys used in the United States is phosphoric acid anodizing (PAA)[9]. Venables and coworkers[8] characterized the surface morphology of the PAA treated surface treatments using the STEM[7-8]. Figure 1 shows an isometric projection drawing depicting the PAA oxide morphology. The figure shows that the oxide consists of a dense barrier layer with a network of hollow well developed hexagonal pores, and whisker like protrusions. The porous layer is approximately 4000Å thick. The microscopic roughness of the oxide film, i.e. whiskers, created by pickling is an essential feature in establishing the bondability of the surface to an adhesive or to a coating. Chemically, the PAA oxide is amorphous $Al_2O_3$, with the equivalent of a monolayer of phosphate ($AlPO_4$) incorporated into the surface film.[8] When exposed to a humid environment, water will adsorb onto the oxide film, changing both the chemical composition and morphology of the oxide.

The morphology of the aluminum surface has been shown to be a strong determining factor in the adhesive bond strength. High surface roughness can provide a high density of locations where the primer or adhesive can form mechanical interlocks with the surface, thereby enhancing adhesion beyond that provided by chemical adhesion. Surface texture on a very fine scale (tens to hundreds of Ångstrom) is provided by the current generation of wet chemical techniques. Similar microscopic scale fine structure can also be generated by ion beam sputtering and deposition techniques[10].

## Ion Beam Enhanced Deposition Process

The IBED process is implemented as shown schematically in Figure 2. The process is carried out in a working chamber held at a vacuum in the $1x10^{-6}$ Torr range. The flux of atoms of the material to be deposited is produced by vacuum evaporation in an electron gun evaporator which is contained within the working chamber. The substrate to be coated is positioned such that it intercepts the flux of filming materials produced by the electron gun evaporator. A broad beam ion source generates a flux of inert atoms, usually Argon, which is directly aimed at the surface to be coated. Thus, the flux of filming atoms plus the secondary flux of Argon atoms strike the substrate surface simultaneously. The two fluxes of atoms can be controlled independently allowing a wide latitude in the ratios of atom arrival rates and energies. This allows complete control of the film deposition and growth environment, and therefore a high degree of control over the morphology of the deposited film.

During the initial phases of film growth, the film atoms can be mechanically mixed into the substrate surface, thereby significantly improving the film adhesion to the substrate. After the substrate surface is sufficiently doped with the film atoms to effect excellent adhesion, a contiguous film can then be grown from the substrate surface. The morphology of this film can be determined by controlling the energies of the respective film and augmenting ion fluxes.

Based on the present knowledge of required surface structure and morphology for good adhesion, namely a large surface area for mechanical anchoring and physical/chemical adhesion, the aluminum alloy surfaces were cleaned and coated using the IBED process. Test specimens were prepared similar to those prepared with pickling and anodizing, and subjected to mechanical testing. Durability tests were conducted after iterative testing to determine the resistance of the oxide surface film to corrosive environments.

## EXPERIMENTAL PROCEDURES

In the first section, the non chemical technique (IBED) to pretreat aluminum alloy 2024-T3 for adhesive bonding is described. In the following sections the test procedures comparing IBED with the standard chemical pickling and anodizing (PAA) process are presented.

## Ion Beam Enhanced Deposition

The oxide films formed on the surfaces of aluminum alloys must satisfy three criteria in order to promote strong adhesive bonding. These criteria are as follows:

1) The oxide films must adhere well to the aluminum alloy substrate,
2) The oxide films must be water and corrosion resistant, and
3) The outermost layers of the surface films must have a morphology that promotes adhesive bonding.

Two different types of IBED oxide film structures were deposited on aluminum alloy 2024-T3 substrates and examined. In both structures, the oxide films were initially ion beam mixed into the alloy substrate to promote strong oxide-substrate adhesion. In both structures, the bulk of the aluminum oxide ($\alpha$ $Al_2O_3$) film deposited was grown under the influence of a high energy inert (Argon) augmenting ion flux. This produced a dense microcrystalline (amorphous) oxide film, with good corrosion resistance . In the first type of structure the outer surface was designed to retain the morphology of the bulk oxide itself. This outer surface, which is micro-crystalline or amorphous, may be smooth and may not have the micro roughness necessary for good adhesive bonding.

A second type of IBED oxide film structure was designed and deposited such that the outer surface presented a larger grained crystalline surface. In this case, the last few layers grew as larger grained alumina ($\alpha$ $Al_2O_3$), and presented a surface for adhesive bonding that has a crystalline, as opposed to a mostly amorphous structure.

## Adhesive Bonding and Testing

Immediately following the various surface treatments, the surfaces were primed with the epoxy polyamide primer Cyanamid BR 127, and were adhesively bonded with the epoxy polyamide adhesive Cyanamid FM 73. Per manufacturer's instructions, the adhesive bonding was accomplished at a pressure of 40 psi and a temperature of 120°C. Adhesive bonding was accomplished over a period of 75 minutes.

## Mechanical Testing

In order to assess the initial mechanical strength of the adhesive bonds, standard peel tests were conducted.

### Peel Testing

The floating roller peel test (ASTM D 3167)[11] is intended to determine the relative peel resistance of adhesive bonds between one rigid adherend and one flexible adherend. Due to the nature of the specimen configuration and loading procedure the highest stresses are exerted on the interface between the flexible adherend and the adhesive which makes this test well suited to evaluate the quality of surface treatments. In this program, the flexible adherend was 0.025 inch thick 2024-T3 sheet with the various surface treatments, whereas the rigid adherend was the same for all tests, namely, 0.063 inch thick 2024-T3 sheet with $HNO_3$-HF pickling treatment.

## Durability Testing

In order to evaluate the effect of aggressive environments on the durability of the surface oxides, various coated and uncoated test coupons were exposed to a 100% relative humidity (RH) water fog and a 5% NaCl salt fog environment (ASTM B-117)[12]. These environments were selected because of their different effects on the oxide film. Specifically, water is known to have a potential detrimental effect on aluminum oxide by hydration resulting in disbonding and subsequent adhesive failure, with no or very little contribution of corrosion to the failure. Salt condensate, on the other hand, is extremely corrosive, and the failure mode of bonded or coated structures exposed to such an environment will be corrosion of the adherend or substrate.

Bare coupons were exposed to the water fog and NaCl salt fog environments in order to determine the resistance of $HNO_3$-HF pickled, PAA treated and IBED treated test coupons to water and chloride salts. The coupons were inspected and photographed at 24 hour intervals. The bare treated coupons were exposed to the salt fog for 48 hours and to the water fog for 288 hours.

In addition to exposure of the treated bare coupons, primer coated and scribed coupons were exposed to the two environments. The PAA and

IBED treated panels were coated with BR 127 primer, which was applied with a soft brush. After curing of the primer, the coupons were scribed diagonally with a scalpel according to ASTM D 1654[13]. The scribed coupons were inspected and photographed at 24 or 48 hour intervals up to a total exposure time of 336 hours.

## RESULTS

The results of this investigation are divided into two separate sections: (1) the effect of surface treatments on the initial mechanical strength, and (2) the durability of some selected surface treatments.

## Mechanical Strength

Aluminum alloy panels were pickled, using the $HNO_3$ - HF and the FPL processes, and phosphoric acid anodized. The results of mechanical strength tests of the chemically treated panels served as reference for the mechanical strength of ion beam cleaned, and IBED treated panels. The results of the mechanical strength testing of aluminum 2024-T3 panel with these treatments are presented in the following sections.

### Pickling And Phosphoric Acid Anodizing

The peel strength of the pickled surfaces show relatively low peel values for the $HNO_3$ - HF treated surfaces with an average peel strength of around 25 lbs/inch, with FPL etched specimens yielding higher peel strengths, ranging from about 25 to 45 lbs/inch. High peel strengths were obtained on PAA treated specimens. Figure 3 which shows a typical peel diagram, indicates peel strengths of phosphoric acid anodized specimens in the range of 70-90 lbs/inch. These values are well above the minimum peel strength specified by the manufacturer for the FM 73 adhesive.

### Ion Beam Enhanced Deposition

The IBED film with a dense microcrystalline (amorphous) morphology had a very smooth outer surface and provided little mechanical anchoring for adhesive bonding. Thus, the peel tests resulted in relatively low peel strength value. The IBED film with the larger grained crystalline outer

surface was much rougher allowing more mechanical anchoring. This treatment resulted in high peel strengths as shown in Figure 4.

## Durability

The durability of an adhesive bond or organic coating interface is an essential characteristic of an adhesively bonded or painted structure. In order to assess the corrosion resistance of the different oxide films and the durability of adhesive/organic primer - aluminum oxide interface, testing in a water fog and a 5% NaCl salt fog environment was performed.

PAA and IBED treated, uncoated coupons and PAA and IBED treated coupons, coated with BR 127 primer and scribed, were exposed to the water and salt fog environments.

### Uncoated Coupons

The treated, uncoated specimens exposed to the water fog were inspected and photographed at frequent intervals. As indicated in Figure 5, the PAA treated surface is not resistant to the wet environment. Pitting attack was observed after as little as 48 hours of exposure. On the other hand, IBED treated surfaces (both with the 2000 Ångstrom and 5000 Ångstrom thick oxide film) resisted the wet environment much longer, and only after 120 hours of exposure some signs of pitting was observed.

Similar specimens were exposed to the 5% NaCl salt fog. The photographs in Figure 6 clearly indicate pitting of the pickled and anodized surfaces after only 5 hours. After 48 hours corrosion was widespread on these surfaces. The IBED treated surfaces showed much higher resistance to the salt fog with some minor attack occurring after 24 hours. Even after an exposure time of 48 hours, pitting corrosion on the IBED surfaces was relatively light.

### Coated Coupons

Treated test coupons were coated with the epoxy polyamide primer BR 127. After curing, they were scribed with a sharp instrument such that the substrate metal was exposed. This test provides a good indication of

the quality of adhesion between the aluminum oxide and the primer. Figure 7, which show photographs of IBED treated and anodized coupons exposed to water and salt fog, demonstrate that the IBED treated coupons resist the wet environment much longer than the anodized coupon. Corrosion of the anodized panel started only after 24 hours and spread rapidly under the coating. Corrosion was also found in the grooves of the IBED treated panel, but underfilm corrosion was observed only after an exposure time of 216 hours.

## DISCUSSION

The results of this work have clearly demonstrated the feasibility of Ion Beam Enhanced Deposition (IBED) as a non chemical alternative to Phosphoric Acid Anodizing (PAA) as pretreatment for adhesive bonding. The program has succeeded in developing a surface that has high mechanical strength, i.e. peel strength, which is equivalent to that obtained by PAA. Moreover, the corrosion resistance of the IBED treated surface exceeded that of the PAA treated surface.

The parameters that are essential for good adhesion and bond line durability were defined. The IBED process allowed the formation of a highly dense amorphous aluminum oxide with no distinct interface between the aluminum alloy substrate and the aluminum oxide which results in very strong bonding between the alloy and the oxide. In order to achieve a surface that would provide mechanical anchoring along with durability, the IBED aluminum oxide film was deposited with a large grained crystalline outer surface thus providing good mechanical anchoring features. The oxide deposition and growth parameters used to achieve good adhesive and durability properties, were as follows:

1) Clean the surface with a degreasing medium as good as or better than acetone-methanol.

2) Apply a 5000 Ångstrom thick aluminum oxide film directly onto the cleaned surface, having a large grained crystalling outer surface.

3) Following the IBED treatment, the vacuum chamber is backfilled with dry nitrogen gas, followed immediately with priming of the surface.

It was suspected that the above described surface was susceptible to water uptake and subsequent hydration, which could destroy the anchoring features of the surface. To minimize exposure of the oxide surface to humid air, the processing chamber was back filled with dry nitrogen, after which the part surface was immediately primed with the epoxy polyamide primer. Once the surface was primed, no effect of humidity or water on the bondability of the surface was found.

Although the IBED process was proven feasible, the process parameters need to be refined, and a mechanistic understanding of the growth of both the amorphous barrier layer and the crystalline top layer is required to implement this procedure with a high level of confidence. Also, the parameters for scaling up the process such that full scale aircraft components can be treated, need to be defined such that implementation of the process can proceed at as low a risk as possible.

## ACKNOWLEDGEMENT

This work was performed under U.S. Air Force Contract No. F33615-93-C-5323 which was administered under the technical direction of Mr. Theodore J. Reinhart, WL/MLSE.

## REFERENCES


1. F. Keller, M. S. Hunter, and D. L. Robinson, "Structural Features of Oxide Coatings on Aluminum," J. of Electrochemical Society, September, 1953, pp. 411-419.

2. P.F.A. Bijlmer, "Influence of Chemical Pretreatments on Surface Morphology and Bondability of Aluminum," J. Adhesion, 1973, Vol. 5, pp 391-331.

3. T. P. Remmel, "Characterization of Surfaces Prior to Adhesive Bonding," Report No. NOR-76-58, July 1976, 92pp, Northrop Corp, Hawthorne, CA.

4. R. E. Herfert, "Fundamental Investigation of Anodic Films on as a Surface Preparation for Adhesive Bonding," Report No NOR-76-101, August, 1976, 111 pp, Northrop Corp, Hawthorne CA.

5. W. L. Russell and C.A.L. Westerdahl, "Characterization of Chromic-Acid Anodized 2024-T3 Aluminum Adherents," Report No. ARLCD-TR-77040, September 1977, 35 pp, Army Armament Research and Development Command, Dover, NJ.

6. T. Smith, "Surface Treatment for Aluminum Bonding," Report No. SC 5180. 17FTR, October 1979, 204 pp, Rockwell International, Thousand Oaks CA.

7. J. D. Venables, D. K. McNamara, J. M. Chen, and T. S. Sun, "Oxide Morphologies On Aluminum Prepared for Adhesive Bonding Applications of Surface Science," Vol 3:1, 1979, p 88.

8. T. S. Sun, G. D. Davis, J. D. Venables, and J. M. Chen, "Effects of Surface Morphology and Chemical Composition on the Durability of Adhesively Bonded Aluminum Structures," Final Report MMLTR81-45C, October 1981, Martin Marietta Corp. Baltimore MA, pp 34.

9. D. B. Arnold, and C. S. Carter, "Service History of Phosphoric Acid Anodized Aluminum Structure," 27th National SAMPE Symposium, 1982, Asuza, CA p. 769.

10. Radiation Effects On Solid Surfaces, Manfred Kaminsky, Ed., American Chemical Society (Advances In Chemistry Series #158), Washington D.C., 1976, pp. 1-63.

11. "Standard Test Method for Floating Roller Peel Resistance of Adhesives," ASTM D3167-76 (1986).

12. Standard Method of Salt Spray (Fog) Testing, ASTM, B117-85.

13. "Evaluation of Painted or Coated Specimens Subject to Corrosive Environments," ASTM D1654 (1984).

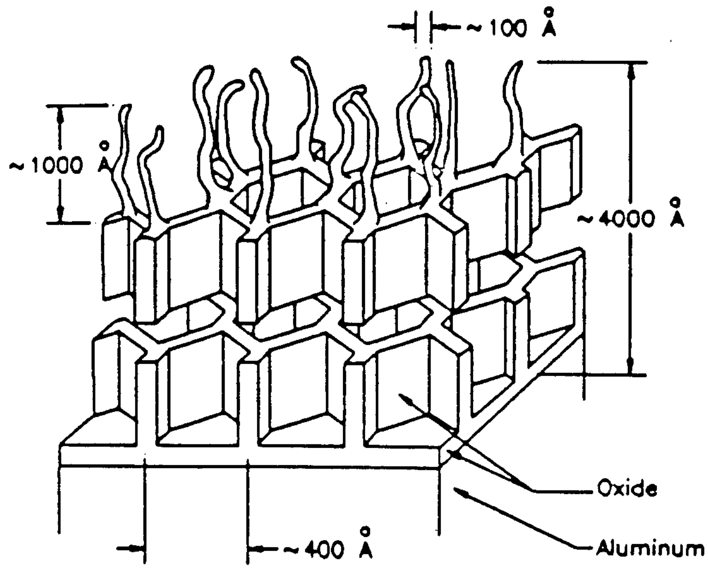



Figure 1. Schematic Representation of Oxide Morphology on a Al Surface After Phosphoric Acid Anodizing

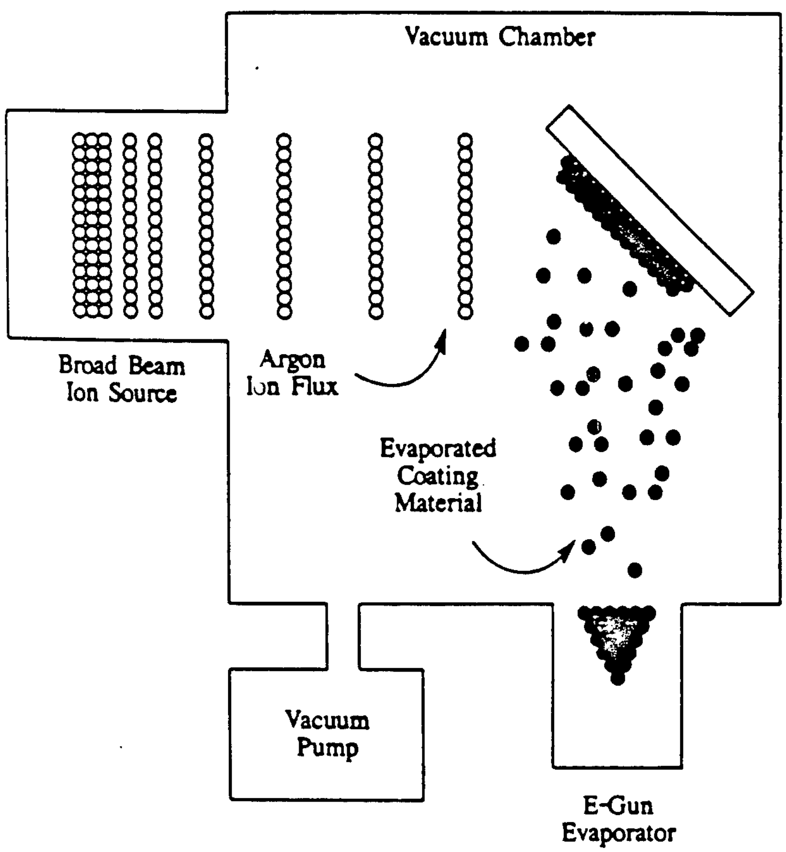



Figure 2. Schematic Drawing of Ion Beam Enhanced Deposition (IBED Process)

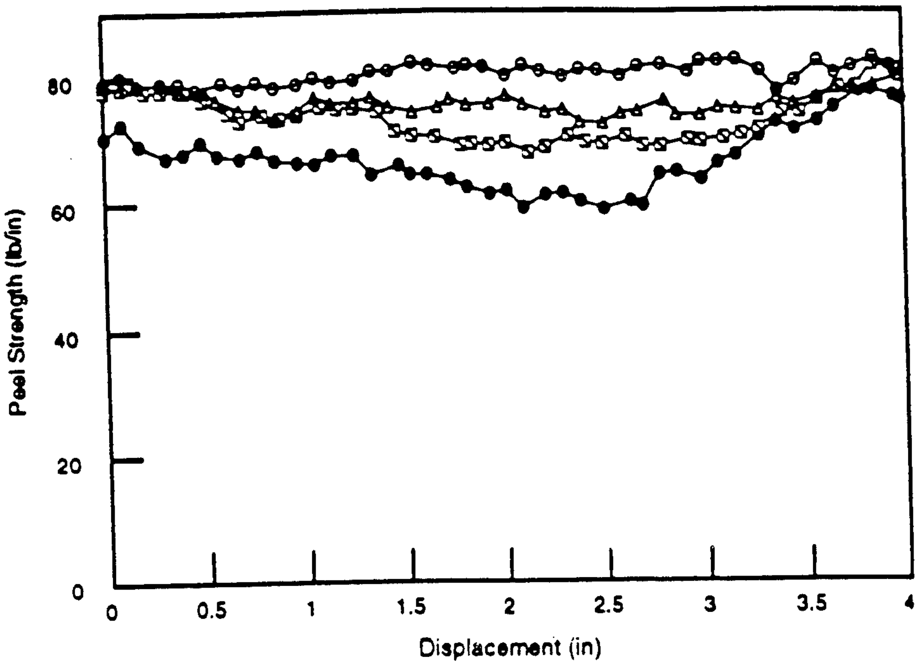



Figure 3. Peel Strength Diagram of Aluminum Alloy 2024-T3 with PAA Treated Surface

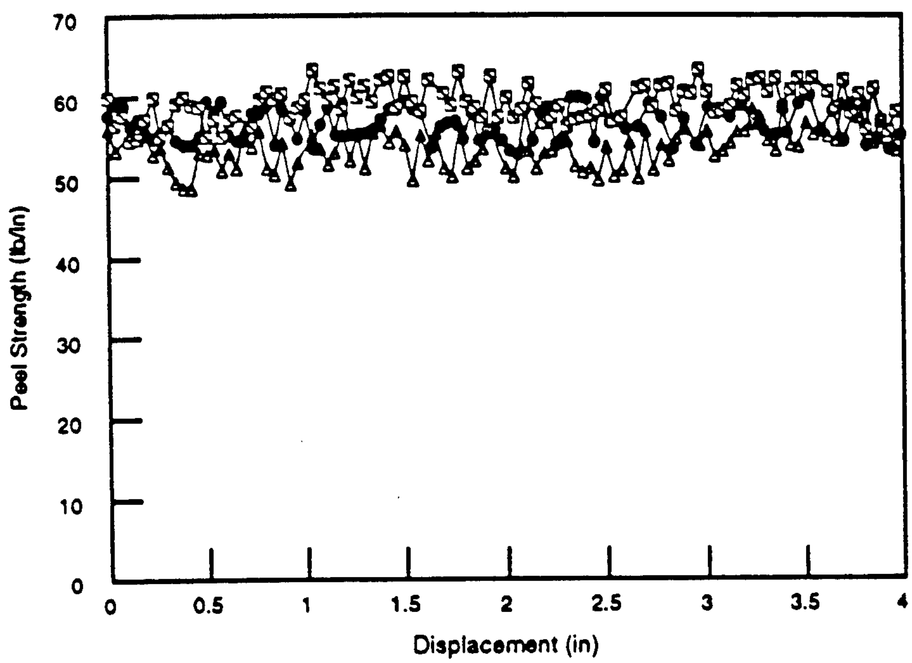
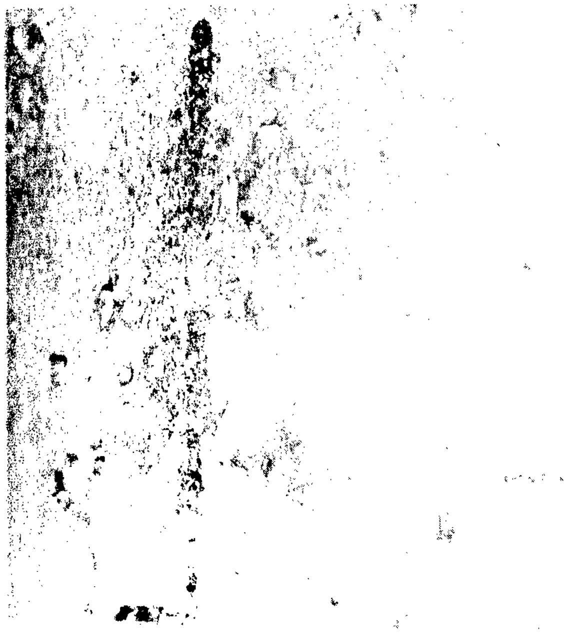
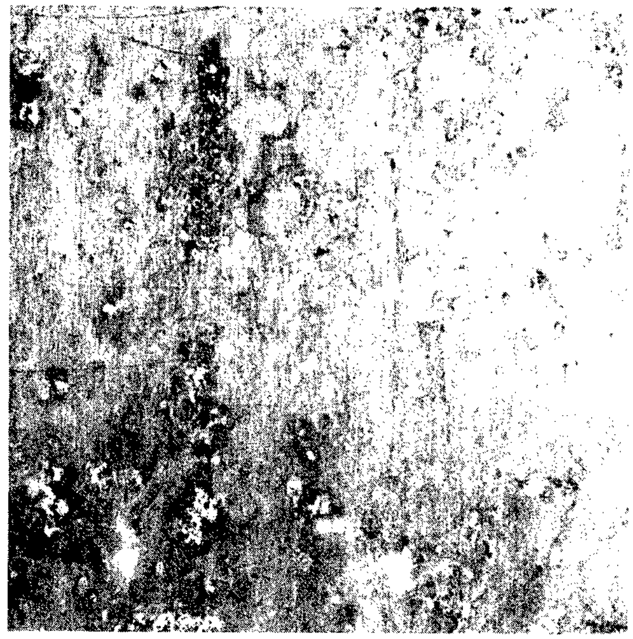



Figure 4. Peel Strength Diagram of Aluminum Alloy 2024-T3 with a 4000Å IBED Barrier Film and a 1000Å Crystalline Top Film (After the Treatment the Vacuum Chamber was Backfilled with Dry $N_2$ Gas and the Surface was Primed Immediately)



**PAA Bare - 48 Hours**
**100% RH**



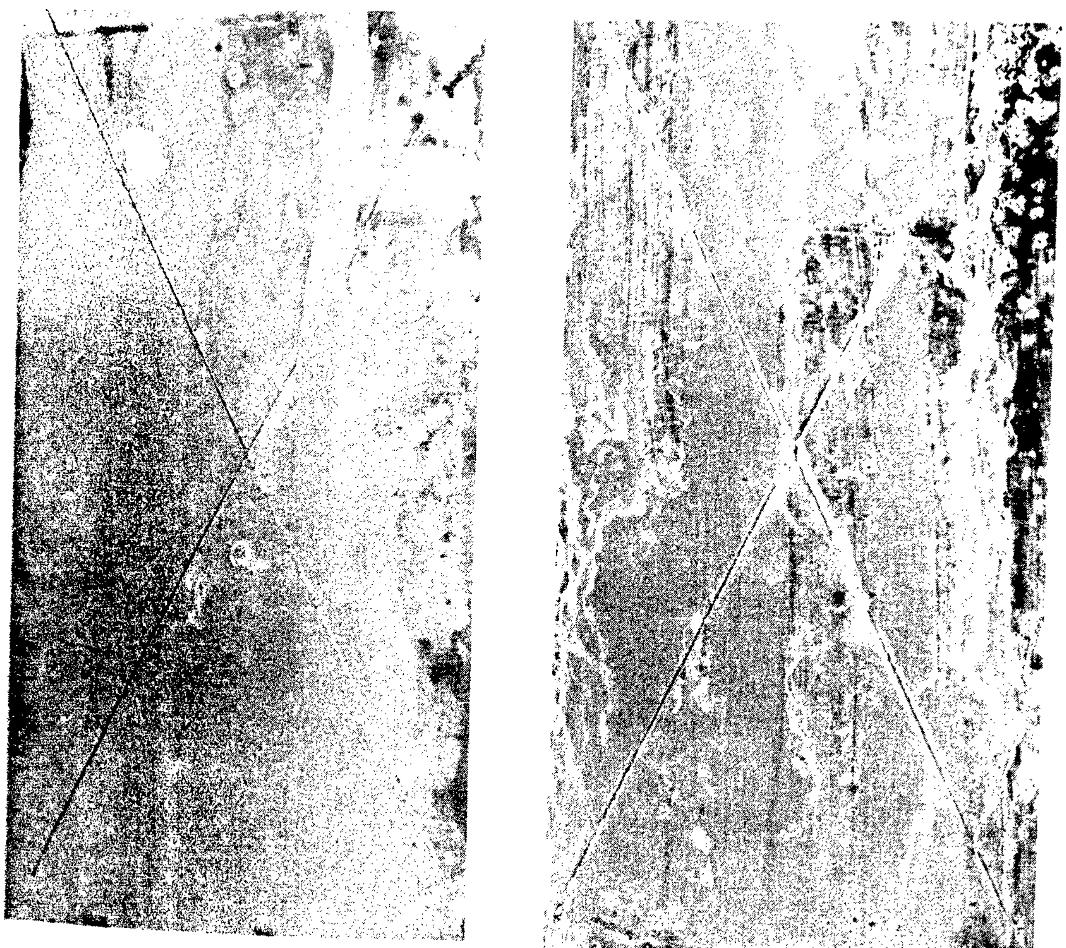
**PAA Bare - 120 Hours**
**100% RH**

**5000 IBED Bare - 48 Hours**
**100% RH**

**5000 IBED Bare - 120 Hours**
**100% RH**

Figure 5. Photographs Of PAA And IBED Treated Aluminum Alloy 2024-T3 Exposed To Water Fog For 48 Hours And 120 Hours, Respectively

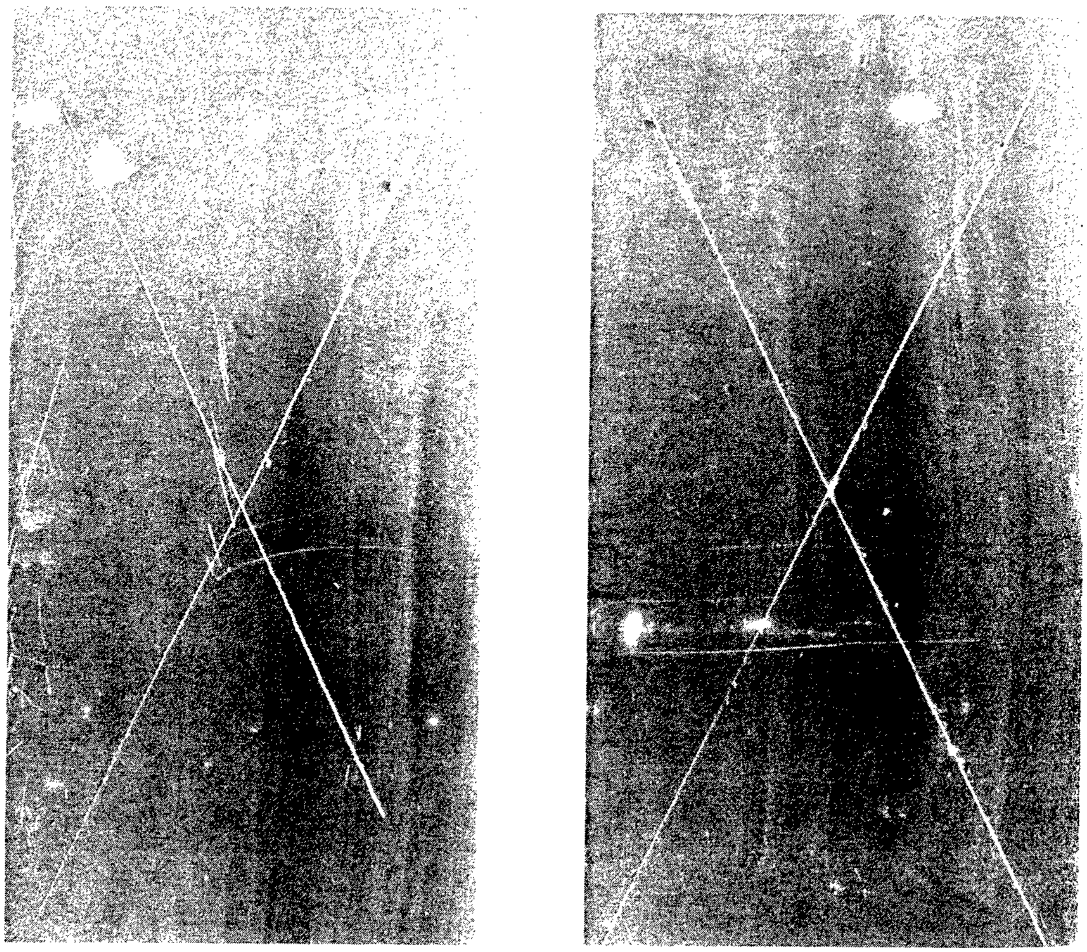

Figure 6. Photographs Of PAA And IBED Treated Aluminum Alloy 2024-T3 Exposed To A 5% NaCl Fog For 48 Hours



**PAA Water**

**PAA - 5% NaCl**

Figure 7. Photographs Of PAA Treated Aluminum Alloy 2024-T4 Coated With BR127 Primer And Scribed After 216 Hour Exposure To Water And Salt Fog, Respectively



**IBED Water** **IBED - 5% NaCl**

Figure 7, Continued.
Photographs Of IBED Treated Aluminum Alloy 2024-T4 Coated With BR127 Primer And Scribed After 216 Hour Exposure To Water And Salt Fog, Respectively